75. The Crystal and Molecular Structure of rac-15-Cyano-1,2,2,7,7,12,12-heptamethyl Corrin Hydrochloride, Metal Free Corrin

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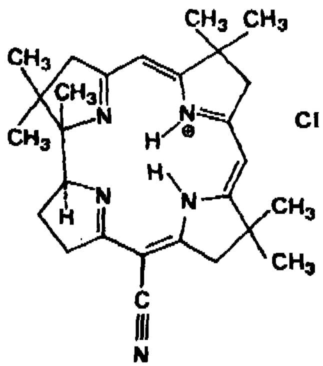
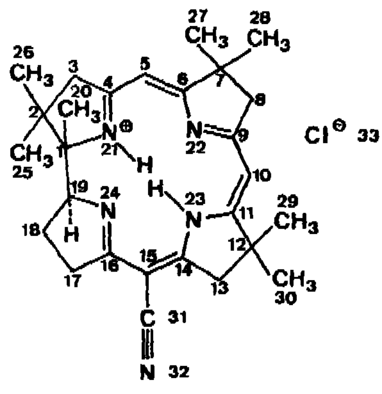
Summary. The crystal structure of a metal free corrin hydrochloride synthesised by *Eschenmoser & Fischli* has been found by X-ray analysis. The crystals are monoclinic and contain ethanol of crystallisation; $a = 10.84$ Å, $b = 12.04$ Å, $c = 26.04$ Å, $\gamma = 120.4$ in space group $P2_1/a$. The structure was determined by direct methods and refined to $R = 0.076$ for 3252 statistically significant reflections with $\theta < 70°$ (Cu Kα). The A ring is found to be markedly displaced from the mean plane of the other three rings; hydrogen atoms are observed in difference electron density maps to be bonded to N21 and N23 of the nucleus. Details of the shape and dimensions of the nucleus are discussed.

Although cobalt free corrinoid compounds have recently been isolated from photosynthesizing bacteria [1], it has so far been impossible to remove, or substitute, another metal ion for the cobalt in the naturally occurring series without destroying the corrin ligand system. The preparation and isolation of the metal free synthetic corrin shown below by *Eschenmoser & Fischli* [2] gave suitable crystals for a structure analysis of this new type of corrinoid.



I

Structure given by *Eschenmoser & Fischli*



II

Crystal structure determined and atomic numbering system

Experimental. – Crystals of the compound precipitated from a mixture of ethanol, ethyl acetate and hexane were kindly supplied by Professor *A. Eschenmoser*. The crystals supplied were orange red, pleochroic and plate like (orange when viewed perpendicular to the face of the plate, the (001) face, and red when viewed parallel to the face of the plate, the (100) face). Many of

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them were easily seen to be twinned because of the sharp colour change from red to orange across a line parallel to the longest edge of the crystal, the a axis direction.

Crystal Data. – $C_{27}H_{38}ClN_5$, C_2H_5OH, M = 512.2, Monoclinic (first setting, unique axis c), $a = 10.84 \pm 0.01$ Å, $b = 12.04 \pm 0.01$ Å, $c = 26.04 \pm 0.02$ Å, $\gamma = 120.4 \pm 0.1°$, V = 2943 Å^3, Dm = 1.17, Z = 4, Dc = 1.16, F(0,0,0) = 1104, Space Group $P2_1/a$ (C_{2h}^5 No 14 – Non standard setting) CuKα radiation, Ni filter, $\lambda = 1.5418$ Å, Dimensions of crystal used in data collection 1.2 mm × 0.7 mm × 0.2 mm, Crystal mounted about the a axis.

The data were collected using a *Hilger & Watts* automatic 4-circle diffractometer by 0.8° $\omega/2\theta$ scans. One quadrant of data in that region of reciprocal space given by h ≥ 0, l ≥ 0, $\theta \geq 70°$ was collected, corrected for absorption using the method suggested by *North et al.* [3] and for *Lorentz* and polarisation effects in the usual manner. This yielded a final set of 3252 independent reflections used in the structure analysis whose intensities were greater than twice their standard deviations (σ_1) calculated from counting statistics. Normalised structure factors, E(hkl), as defined by *Karle & Hauptmann* [4] were calculated using an overall temperature factor and absolute scale factor for the data derived by *Wilson*'s method and then rescaling to give an average E^2 value of 1.

Structure Solution and Refinement. – The structure was solved using a programme written by Mr. *O. J. R. Hodder* of this laboratory for the KDF9 computer which applied the symbolic addition procedure developed by *Karle & Karle* [5] as follows. The largest 800 Es, those with |E| > 1.32, were input and the 6,900 triple products holding between them with a probability greater than 0.90 stored. The minimum probability at which a sign would be accepted as determined from a Σ_2 (or a Σ_1) relationship was set at 0.992. The programme accepted signs one by one, each new sign always being the one indicated with the highest probability at that stage. Once a reflection had been given a sign it kept that sign throughout the rest of the process. The programme fixed the unit cell origin by giving positive signs to the three reflections, 301 (|E| = 4.56); 012 (|E| = 4.17); and 201 (|E| = 3.51), and allocated the three reflections, $2\,3\,1\bar{1}$ (|E| = 3.27); $3\bar{1}1$ (|E| = 2.94); and $6\bar{8}16$ (|E| = 3.06) symbolic signs A, B and C respectively in the course of the symbolic addition. Signs were determined for 462 reflections in terms of these three symbols by the end of the process. Further, out of the eight possible solutions corresponding to the two possible signs for each of A, B and C, that given by A ≡ + B ≡ – C ≡ + was computed as giving the most internally consistent set of signs in the symbolic addition process. Using this assignment of A, B and C signs were computed at the 0.88 probability level for 680 reflections and used to calculate an E map. The probability criterion was reduced at this stage in order to improve the quality of the resulting E map by including as many signed Es as possible in the *Fourier* synthesis. A later comparison showed that only eight Es were given wrong signs in this process, all of which were determined with a probability less than 0.93.

The resulting E map was easily interpretable, out of the highest 34 peaks in the map 33 were found to represent atomic positions consistent with formula I and only one, the 32nd in order of magnitude, was spurious. The only atomic position not found was one of the methyl groups on C(12). The highest peak clearly gave the position of the chloride ion which seemed to be linked to N(21) *via* an extra intermediate atom through a hydrogen bond network. This atom lying approximately 3.0 Å from the chlorine ion and N(21) was provisionally identified as an oxygen atom belonging to the ethanol used in the crystallisation. Structure factors were calculated for the 32 atomic positions found, omitting the oxygen as a check against its being spurious, and an F obs. map generated using the calculated signs. This map confirmed the positions of the 32 input atoms and had additional peaks at positions corresponding to the ethanol oxygen atom, the missing C(12) methyl group and the 2 remaining ethanol carbon atoms. The latter 2 peaks were low in height (2.0 e/Å^3 and 1.4 e/Å^3) and rather diffuse, indicating some disorder in the positions of these atoms.

The atomic parameters of this trial structure were refined by block diagonal least squares. The quantity minimised was

$$M = \sum_{h} w(h) (|F_0(h)| - K|F_c(h)|)^2 = \sum_{h} w(h) \Delta^2(h)$$

where K was the refined overall scale factor and w(*h*) was a weight given to each $F_0(h)$ and was set equal to unity except in the final stages of the refinement. The structure was refined first for 4 cycles using isotropic thermal parameters and then for a further 3 cycles using anisotropic thermal parameters at which stage R was 0.095. A difference map was calculated at this stage with an e.s.d. in the electron density at a general position of 0.14 e/Å^3. The positions of peaks of height greater than 2 e.s.d.'s (0.28 e/Å^3) were, with one important exception, in accordance with hydrogen atom positions of formula I. The only other peaks were three of height 0.30 e/Å^3 in the region of the solvent carbon atoms and two of height 0.35 e/Å^3 near

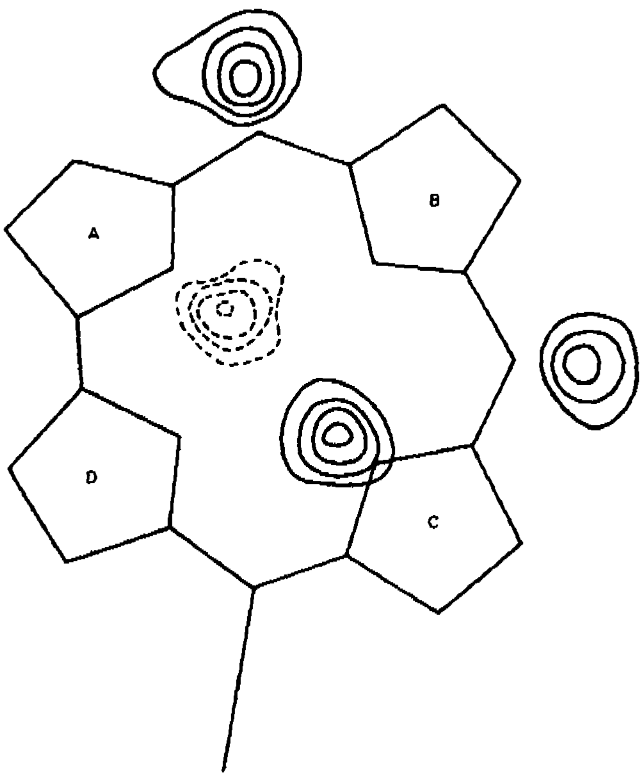


Fig. 1. *Difference map drawn through the plane of N(22), N(23) and N(24)*. Contours at 0.1 e/Å^3. Dotted contours indicate the projection of H N(21) onto this plane.

the chlorine ion indicating some residual disorder in these positions. As a result of this disorder the only hydrogen atom of the ethanol solvent molecule located was the hydroxyl hydrogen forming the hydrogen bond between the oxygen and the chlorine ion.

The major difference from formula I was that no hydrogen atom was found bonded to N(22). Instead one was found 0.81 Å from N(21) directly between N(21) and the ethanol oxygen with a peak height of 0.46 e/Å^3. This is illustrated in Fig. 1. The only hydrogen atoms not clearly located at this stage were those bonded to methyl carbon atoms 28, 29 and 30. An examination of the difference map in the regions around these atoms however showed a number of peaks ranging in height from 0.22 to 0.28 e/Å^3 giving rather distorted methyl hydrogen positions. These 9 hydrogen atoms were therefore placed geometrically and included with the 28

Table 1. *Corrin Hydrochloride Refined Atomic Coordinates* (e.s.d.'s × 10^4 in brackets)

Atom Type	Atom No.	x/a	y/b	z/c
Cl	33	–0.0288 (2)	0.5468 (2)	0.1609 (1)
N	21	0.1907 (4)	0.3062 (3)	0.0351 (1)
N	22	0.3167 (4)	0.3682 (4)	0.1354 (1)
N	23	0.3428 (5)	0.6133 (4)	0.1272 (1)
N	24	0.3331 (4)	0.5570 (3)	0.0268 (1)
C	1	0.1819 (4)	0.3528 (4)	–0.0169 (1)
C	20	0.0471 (5)	0.3609 (4)	–0.0212 (2)
C	2	0.1875 (5)	0.2481 (4)	–0.0514 (2)
C	26	0.2585 (7)	0.2984 (7)	–0.1038 (2)
C	25	0.0356 (6)	0.1310 (6)	–0.0589 (2)
C	3	0.2740 (5)	0.2066 (4)	–0.0172 (2)
C	4	0.2478 (4)	0.2348 (4)	0.0366 (2)
C	5	0.2842 (5)	0.1929 (4)	0.0822 (2)
C	6	0.3130 (5)	0.2528 (4)	0.1280 (2)
C	7	0.3491 (7)	0.2056 (6)	0.1775 (2)
C	27	0.4876 (9)	0.2042 (9)	0.1720 (3)
C	28	0.2264 (11)	0.0668 (9)	0.1896 (4)
C	8	0.3547 (11)	0.3027 (9)	0.2163 (2)
C	9	0.3432 (7)	0.3995 (6)	0.1843 (2)
C	10	0.3577 (8)	0.5123 (7)	0.2059 (2)
C	11	0.3542 (6)	0.6069 (6)	0.1798 (2)
C	12	0.3783 (7)	0.7347 (7)	0.2010 (2)
C	29	0.2867 (11)	0.7132 (11)	0.2493 (3)
C	30	0.5386 (10)	0.8216 (10)	0.2128 (4)
C	13	0.3349 (7)	0.7906 (6)	0.1561 (3)
C	14	0.3391 (5)	0.7173 (5)	0.1098 (2)
C	15	0.3354 (5)	0.7434 (4)	0.0595 (2)
C	31	0.3352 (6)	0.8590 (5)	0.0464 (3)
N	32	0.3354 (7)	0.9518 (5)	0.0358 (8)
C	16	0.3303 (5)	0.6610 (4)	0.0176 (2)
C	17	0.3176 (6)	0.6870 (5)	–0.0379 (2)
C	18	0.3220 (5)	0.5755 (4)	–0.0649 (2)
C	19	0.3186 (5)	0.4877 (4)	–0.0213 (2)
O	34	0.0067 (6)	0.3400 (5)	0.1059 (2)
C	35	–0.0677 (16)	0.2768 (12)	0.1414 (4)
C	36	–0.0160 (27)	0.3725 (12)	0.1161 (9)

previously located in all future structure factor calculations. The hydrogen atoms were given isotropic temperature factors equal to those of the atoms to which they were bonded at the end of the isotropic refinement. Their positional and temperature factors were not refined and are given in Table 2.

Table 1a. *Corrin Hydrochloride Refined Temperature Parameters* × *10*[4] (e.s.d.'s in brackets)[a])

U11	U22	U33	U23	U31	U12
976 (11)	1456 (14)	522 (6)	– 107 (15)	– 10 (13)	1539 (22)
565 (18)	475 (16)	426 (15)	– 52 (25)	29 (26)	612 (29)
700 (24)	704 (22)	436 (16)	4 (30)	– 73 (30)	851 (39)
722 (24)	684 (22)	601 (20)	– 464 (35)	– 296 (35)	932 (40)
626 (21)	442 (16)	510 (17)	– 99 (27)	– 169 (31)	549 (31)
550 (21)	512 (19)	338 (15)	– 78 (28)	– 26 (29)	637 (35)
514 (22)	654 (24)	508 (20)	– 78 (36)	– 52 (34)	700 (40)
617 (25)	628 (24)	449 (19)	– 321 (34)	– 121 (34)	746 (42)
990 (40)	1080 (41)	438 (21)	– 241 (48)	55 (47)	1377 (71)
717 (33)	692 (29)	924 (37)	– 709 (56)	– 426 (55)	697 (53)
582 (25)	596 (23)	576 (22)	– 208 (36)	– 33 (34)	734 (42)
546 (22)	396 (17)	538 (21)	– 54 (31)	– 40 (34)	502 (34)
679 (27)	500 (22)	611 (24)	146 (36)	– 7 (39)	699 (41)
632 (26)	580 (23)	489 (20)	324 (36)	124 (36)	706 (41)
985 (40)	840 (33)	537 (24)	532 (48)	202 (50)	1131 (63)
1204 (55)	1608 (69)	783 (37)	904 (83)	141 (71)	2014 (110)
1319 (68)	1212 (61)	1127 (54)	1384 (100)	359 (98)	1142 (108)
1800 (84)	1634 (74)	513 (27)	375 (72)	41 (74)	2552 (144)
1020 (41)	1038 (40)	405 (21)	6 (46)	– 98 (46)	1363 (70)
1123 (47)	1287 (50)	437 (23)	– 408 (51)	– 406 (51)	1710 (86)
859 (36)	1009 (39)	522 (23)	– 674 (53)	– 372 (45)	1264 (64)
879 (39)	1187 (46)	867 (36)	– 1238 (72)	– 776 (63)	1524 (77)
1670 (83)	2163 (97)	739 (36)	– 1209 (102)	– 681 (89)	3011 (164)
1225 (66)	1461 (71)	1913 (92)	– 2345 (147)	– 1637 (130)	1893 (122)
867 (38)	886 (36)	942 (38)	– 776 (64)	– 313 (61)	1206 (65)
652 (28)	576 (24)	766 (28)	– 463 (43)	– 263 (45)	754 (44)
562 (25)	479 (21)	854 (31)	– 189 (41)	– 179 (44)	631 (39)
639 (30)	524 (26)	1164 (45)	– 116 (54)	21 (58)	646 (47)
1099 (43)	673 (28)	1582 (59)	148 (66)	238 (79)	1184 (59)
477 (22)	477 (21)	634 (23)	112 (35)	– 34 (36)	477 (35)
756 (32)	698 (27)	717 (28)	411 (47)	60 (47)	886 (51)
612 (26)	640 (25)	511 (21)	281 (38)	26 (37)	509 (43)
516 (21)	499 (19)	442 (17)	– 43 (31)	– 76 (31)	502 (34)
1077 (34)	1191 (36)	706 (23)	113 (46)	410 (46)	1325 (61)
2201 (151)	1445 (88)	1269 (80)	676 (145)	1442 (184)	1340 (194)
3672 (324)	1053 (93)	3424 (283)	1061 (275)	– 10 (498)	1340 (308)

[a]) The temperature factor T is given by the expression
$T = \exp[-2\pi^2 (U_{11}h^2 a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2\,U_{23}klb^*c^* + 2\,U_{31}lhc^*a^* + 2\,U_{12}hka^*b^*)]$

The unit weights refinement converged after a further 3 cycles. Each $F_0(h)$ was given an absolute weight $w(h)$ defined by

$$1/w(h) = \sigma_1^2\,[F_0(h)] + c^2\,|F_0(h)|^2$$

as suggested by *Grant et al.* [6] where σ_1^2 [$F_0(h)$] is the variance in $F_0(h)$ calculated from the counting statistics and c^2 is a constant calculated to be 0.0055 in this case. With these weights the refinement converged after a further 3 cycles. Before the last cycle, 6 reflections with a value of $w(h) \times ||F_0(h)| - |F_c(h)||$ greater than 5 were considered subject to serious non random errors and were given zero weight in the last cycle. On the last round the calculated shifts were all less than 0.5 of the corresponding e.s.d. The final R was 0.076. The final atomic parameters and their e.s.d.'s are given in Tables 1 and 1a.

Observed structure amplitudes and calculated structure factors are given in reference [8]. All calculations were carried out on the Oxford University KDF9 computer using the NOVTAPE system developed by *J. S. Rollett* and improved by *J. Hodder* and *G. Ford*. Scattering factors were taken from reference [7].

Table 2. *H-Corrin Hydrogen Atom Parameters* (not refined)

Atom No.	x/a	y/b	z/c	Uiso
H 1 C 20	−0.0452	0.2768	−0.0064	0.051
H 2 C 20	0.0253	0.3725	−0.0598	0.051
H 3 C 20	0.0646	0.4423	0.0009	0.051
H 1 C 25	0.3702	0.3706	−0.0997	0.067
H 2 C 25	0.2072	0.3392	−0.1260	0.067
H 3 C 25	0.2521	0.2236	−0.1273	0.067
H 1 C 26	−0.0261	0.1592	−0.0830	0.075
H 2 C 26	0.0436	0.0546	−0.0767	0.075
H 3 C 26	−0.0180	0.0938	−0.0225	0.075
H 1 C 3	0.3667	0.2483	−0.0233	0.053
H 2 C 3	0.2475	0.1178	−0.0194	0.053
H 1 C 5	0.2876	0.1055	0.0744	0.056
H 1 C 27	0.4949	0.1472	0.2033	0.100
H 2 C 27	0.5727	0.3040	0.1718	0.100
H 3 C 27	0.5053	0.1554	0.1396	0.100
H 1 C 28	0.2543	0.0257	0.2220	0.127
H 2 C 28	0.1393	0.0818	0.2016	0.127
H 3 C 28	0.2127	0.0042	0.1576	0.127
H 1 C 8	0.2624	0.2601	0.2422	0.099
H 2 C 8	0.4648	0.3474	0.2254	0.099
H 1 C 10	0.3843	0.5182	0.2406	0.074
H 1 C 29	0.1752	0.6580	0.2369	0.105
H 2 C 29	0.3068	0.8079	0.2592	0.105
H 3 C 29	0.3187	0.6703	0.2784	0.105
H 1 C 30	0.5627	0.7802	0.2454	0.120
H 2 C 30	0.5660	0.9206	0.2205	0.120
H 3 C 30	0.6004	0.8274	0.1786	0.120
H 1 C 13	0.4080	0.8832	0.1473	0.074
H 2 C 13	0.2387	0.7698	0.1581	0.074
H 1 C 17	0.2146	0.6790	−0.0429	0.065
H 2 C 17	0.3967	0.7680	−0.0445	0.065
H 1 C 18	0.2466	0.5391	−0.0875	0.059
H 2 C 18	0.4123	0.6078	−0.0842	0.059
H 1 C 19	0.4048	0.4738	−0.0246	0.047
H 1 N 21	0.1687	0.3388	0.0577	0.043
H 1 N 23	0.3367	0.5576	0.1076	0.0504
H 1 O 34	0.0033	0.4045	0.1337	0.071

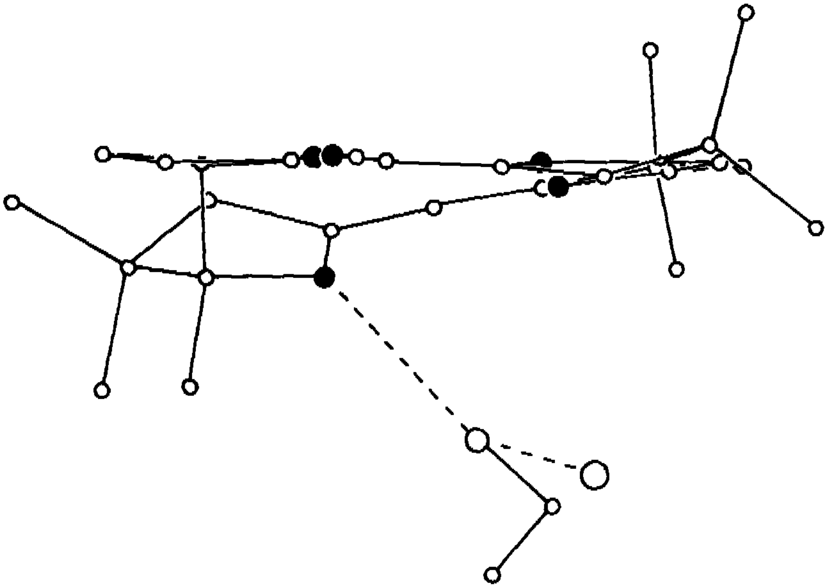


Fig. 2. *Molecule projected onto plane perpendicular to the* b *axis*

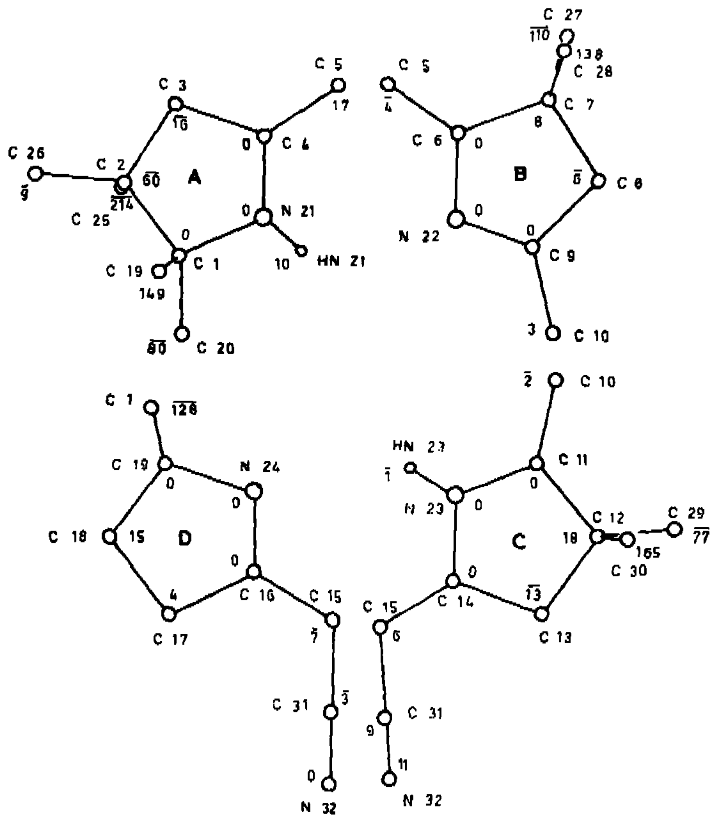


Fig. 3. *Conformations of the five-membered rings.* Deviations of atoms (in Å × 100) from the plane through each nitrogen atom and its two neighbouring carbon atoms are given.

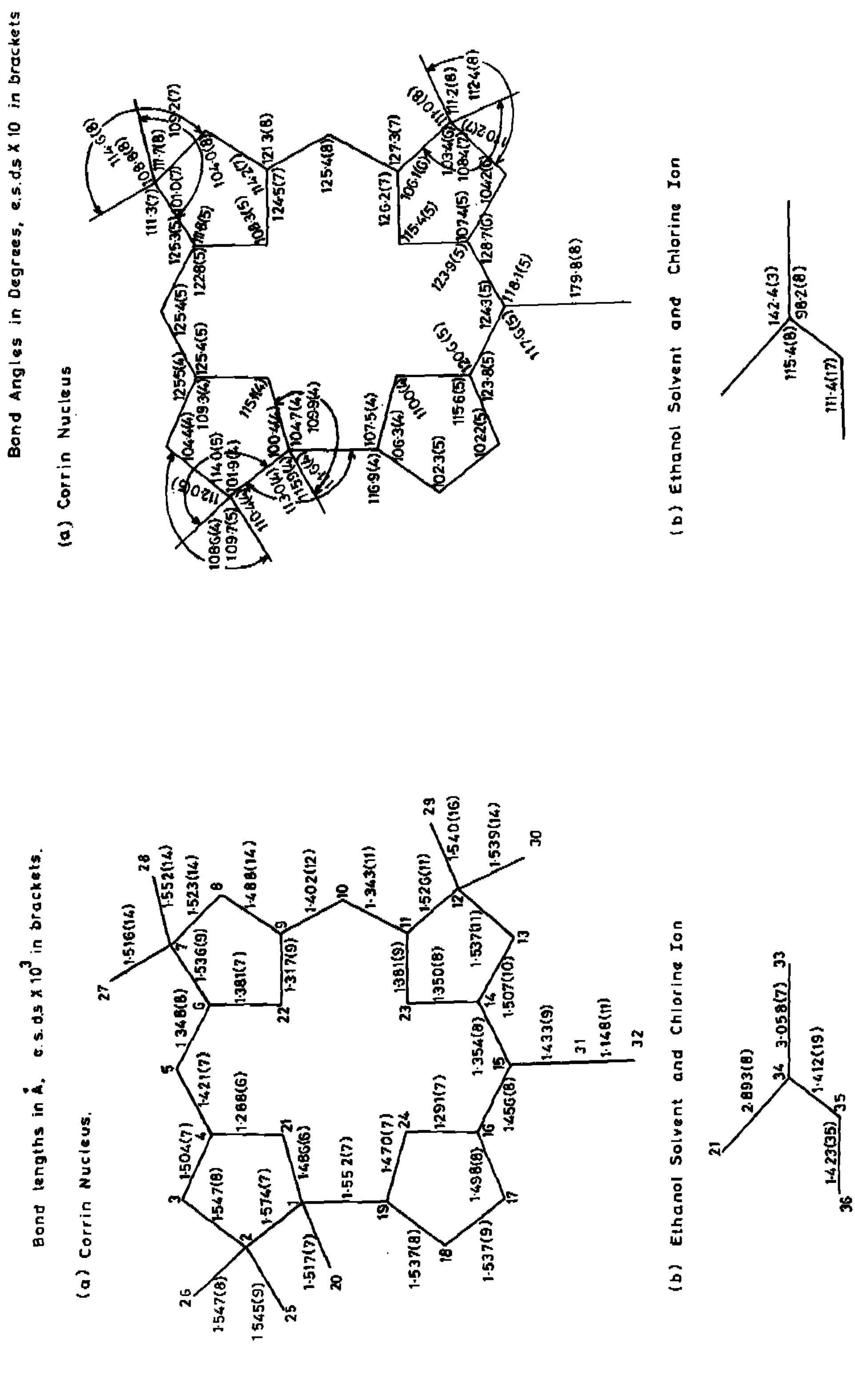


Fig. 4. *Bond lengths, bond angles and estimated standard deviations*

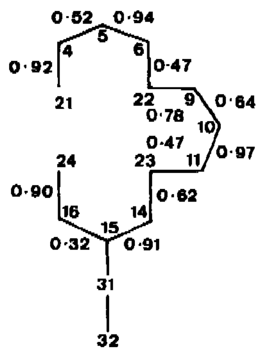
Discussion. – The most obvious feature of the structure as shown below in Fig. 2 is the substantial displacement of the A ring from the almost planar remainder of the molecule, clearly illustrating the 'trans' configuration of the direct link between the A and D rings. The conformations of the 5 membered rings are illustrated below in Fig. 3. The A ring is the least planar of the 4 pyrrole type rings with a root mean square displacement of its 5 constituent atoms from their mean plane of 0.13 Å compared with 0.08 Å for the C ring, 0.04 Å for the B ring and 0.03 Å for the D ring.

Mobile, π, bond orders in the inner conjugated macrocycle were calculated using the linear relationships between bond lengths (τ) and bond orders (p) given by *Dewar & Schmeisung* [9] and *Miller et al.* [10], viz.,

$$\tau = 1.511 - 0.173\ \text{p for sp}^2\ \text{carbon} - \text{sp}^2\ \text{carbon bonds and}$$

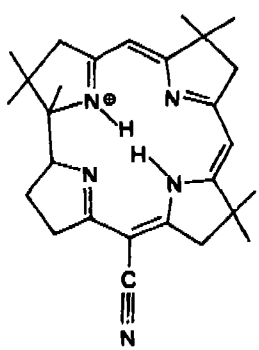
$$\tau = 1.478 - 0.208\ \text{p for sp}^2\ \text{carbon} - \text{sp}^2\ \text{nitrogen bonds.}$$

Bond orders thus calculated are shown below.

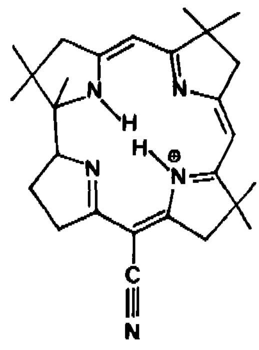


π Bond Orders

There are clearly 6 bonds of almost pure double bond character *i.e.* those with a mobile bond order of 0.90 or larger. The effect of bond delocalisation is shown in the high bond orders and short bond lengths for the formally single bonds C(4)–C(5) and C(9)–C(10) given in formula **II**. The lengths of the C(15)–C(16) bond, 1.456 Å, and the C(15)–C(31) bond, 1.433 Å, when compared with values of 1.465 Å and 1.426 Å for single bonds in cyclo-octatetraene and vinyl cyanide respectively (*Sutton* [11]), imply a substantially smaller degree of bond delocalisation in this part of the molecule.



II



III

On this basis the structure is best represented by the resonance hybrids, II and III, shown below, with II preferred.

The intra-annular bond angles subtended at the two hydrogen-bearing nitrogen atoms, N(21) and N(23), are in both cases slightly more than 115° and are significantly larger than the intra-annular angles at N(22), 108.3°, and N(24), 110°. This is in qualitative accordance with an observation made by *Singh* [12] that for compounds containing nitrogen in six membered heterocyclic rings the intra-annular angle is larger than 120° for hydrogen-bearing nitrogens and smaller than 120° for non-hydrogen-bearing nitrogen atoms. He quotes average figures of 125° for the first type and 116° for the second. The two hydrogen atoms differ geometrically. The hydrogen atom attached to N(23), at 0.82 Å, lies closely in the plane defined by the C ring atoms, N(21), C(11) and C(14) – 0.01 Å away – and closer to N(24) than to N(22) (2.10 Å compared with 2.30 Å). The hydrogen atom attached to N(21) (at 0.81 Å) deviates markedly, 0.10 Å, from the plane of the A ring atoms N(21), C(1) and C(4), in the direction of the ethanol oxygen atom, 2.73 Å away, to which it is bonded.

There are three short intramolecular non bonded interactions in the region of the direct link, viz. C(20)–C(25), 2.88 Å, C(26)–C(19), 2.95 Å and C(20)–C(18), 3.00 Å. It is therefore surprising that the bond angles around C(19), C(1) and C(2) should differ so little from tetrahedral angles; the maximum extra annular deviation occurs for the angles C(1)–C(19)–C(18), 116.9°, and C(2)–C(1)–C(20), 115.9°.

Comparison with Metal Containing Corrins. – The structure most directly comparable with the metal free corrin hydrochloride is the synthetic dicyano-cobalt(III) complex of the same ligand – 1,2,2,7,7,12,12-heptamethyl-15-cyano-*trans*-corrin (dicyano cobalt corrin) whose structure has been recently determined by *Shaffner* [13]. The nickel(II) complex of the closely related ligand, 1,8,8,13,14-pentamethyl-5-cyano-*trans*-corrin chloride, studied by *Dunitz & Meyer* [14] and the natural corrins, such as cobyric acid [15], differ more or less widely in the ring substituents.

The most marked differences between the metal free compound and all these others arise from the release of the restraints imposed by nearly planar coordination of the ring nitrogen atoms around metal ions. The consequent deviation of the A ring from the plane of the other three rings is accompanied by a conformational change; the β-β' bond slopes in the opposite direction to the mean plane of the ring to that found in all metal corrins so far examined. This is the result of a twist around the bond C(1), C(2) which places C(25) nearly axial to the ring, on the same side as C(20), and C(26) equatorial. In the other corrins, the group axial to the ring is on the opposite side to C(20) (compare Fig. 5). The changes are correlated with the more nearly tetrahedral values of the bond angles in this region compared with the metal corrins. In the dicyano cobalt corrins, for example, C(1)–C(19)–C(18) is 122° and the angle C(2)–C(1)–C(20) is 123°; in the Ni(II) corrin the C(1)–C(19)–C(18) is 120°. The observations here confirm the suggestion of *Dunitz & Meyer* [14] that the enlarged angles in the metal corrins reflect strains imposed by the conflict between the metal coordination and the natural staggered arrangement of groups around the carbon atoms. As Table 3 shows, N(21) is significantly closer to N(22) and N(24) in the dicyano cobalt corrin than in the corrin hydrochloride.

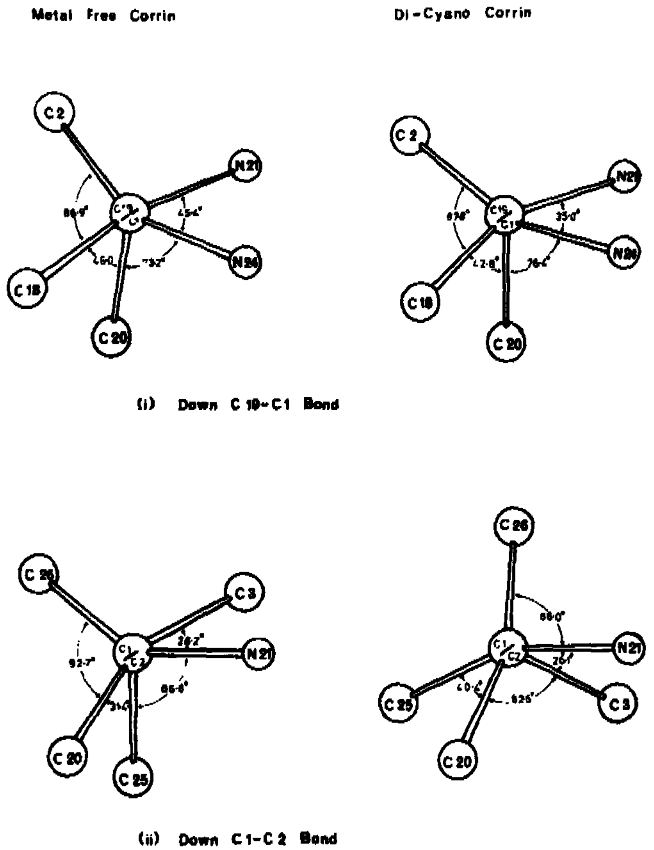


Fig. 5. *Dihedral angles for the metal free corrin hydrochloride and dicyano cobalt corrin about* 1. the C(1) – C(2) bond; 2. the C(1) – C(19) bond

Table 3. *Inner Nitrogen Distances for Two Synthetic Corrinoids*

Contact	Metal Free Corrin (Å)	Dicyano Co Corrin (Å)
21–22	2.87	2.76
22–23	2.83	2.84
23–24	2.69	2.75
24–21	2.61	2.48

The bond lengths observed in the inner conjugated macrocycles of the three compounds are compared in Table 4. The average of these bond lengths is almost exactly the same for the first two and very little longer for the third. One might expect greater deviations from the average in the metal free corrin where there is no metal interacting with the ring conjugation. This is as observed, though the differences are not very marked.

Table 4. *A Comparison between Bond Lengths (in Å) for Three Synthetic Corrinoids*

Bond	Metal Free Corrin (Å)	Dicyano Co Corrin (Å)	Ni(II) Corrin (Å)
21–4	1.288	1.287	1.288
4–5	1.421	1.412	1.436
5–6	1.348	1.341	1.355
6–22	1.381	1.400	1.365
22–9	1.317	1.335	1.361
9–10	1.402	1.385	1.383
10–11	1.343	1.361	1.388
11–23	1.381	1.360	1.367
23–14	1.350	1.361	1.397
14–15	1.354	1.389	1.358
15–16	1.456	1.397	1.429
16–24	1.291	1.287	1.277
Average Bond Length	1.360	1.360	1.367
Mean Square Deviation from Average (Å)	0.00233	0.00157	0.00207

Crystal Packing. – The molecules pack in two layers, almost exactly parallel with the *a* plane at x/a ≈ 1/4 and x/a ≈ 3/4 as shown in Fig. 6 and 7. The ethanol solvent and chlorine ion, closely associated with one molecule, occupy the gap between two other molecules in the parallel layer. Within each layer, the molecules are close packed in the b axis direction while the gap between the successive molecules in the direction of the c axis accommodates the chlorine ion and ethanol.

The figures show the hydrogen bonded connections of the chlorine ion through the ethanol oxygen to N(21) of one molecule. The ion makes other close non bonded contacts to the atoms of the C ring of the same molecule, Cl(33)–C(13), 3.53 Å,

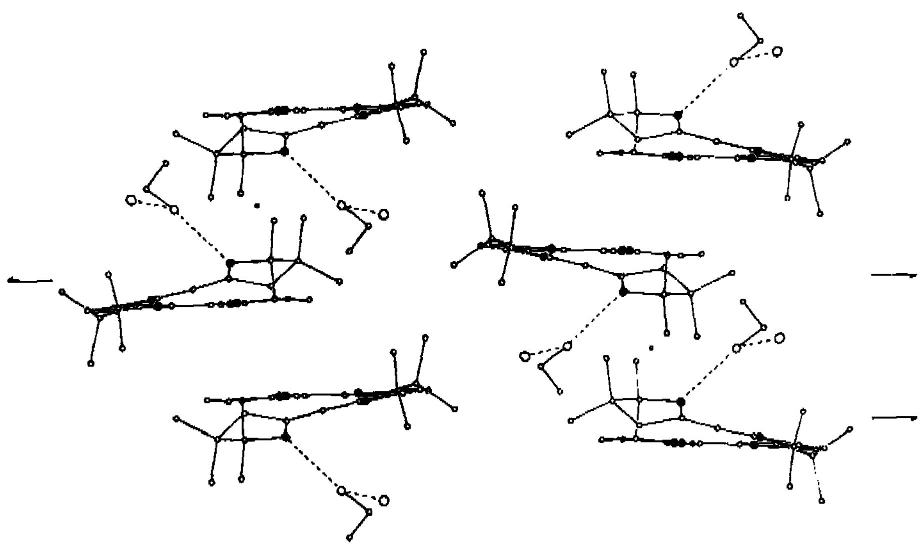


Fig. 6. *Molecular packing viewed along the* b *axis*

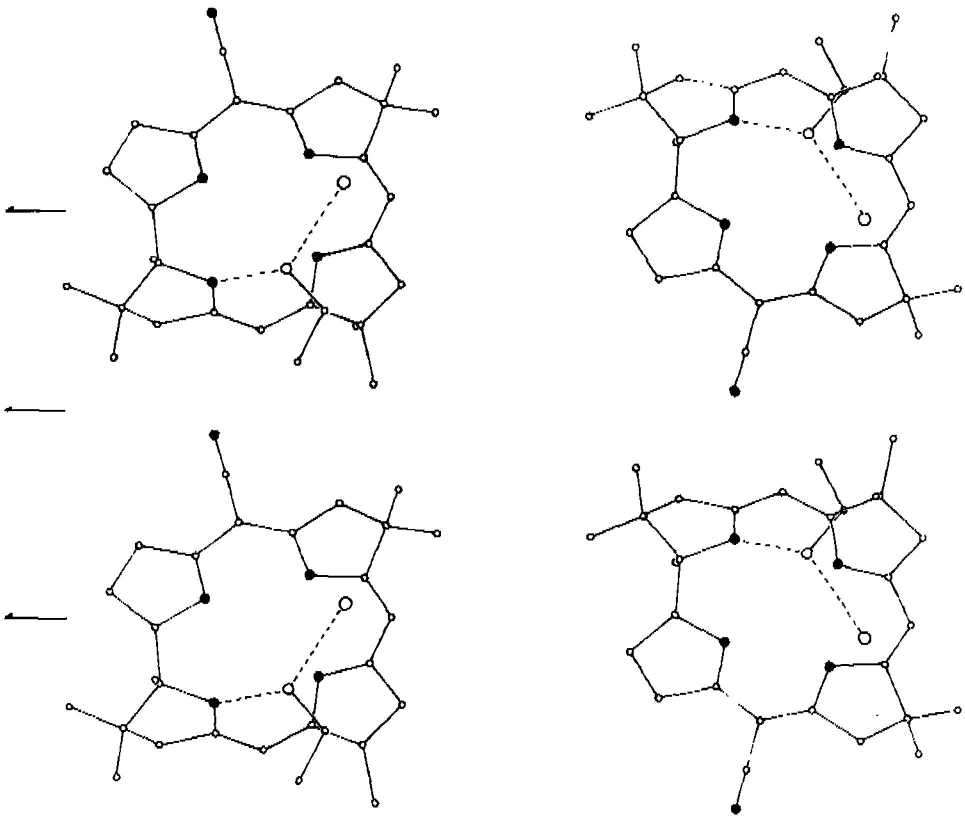


Fig. 7. *Molecular packing viewed along the* a *axis*

Cl(33)–C(14), 3.69 Å, Cl(33)–C(12), 3.95 Å, Cl(33)–C(29), 3.75 Å, Cl(33)–C(11), 3.87 Å, Cl(33)–N(23), 3.79 Å. Close contacts with atoms of two other molecules are Cl(33)–C(10), 3.63 Å, Cl(33)–C(18), 3.71 Å and Cl(33)–C(20), 3.86 Å.

The molecular packing found in these crystals is very favourable for the study of the directional spectroscopic properties of the corrin nucleus. Such a study could yield further valuable information on the electronic properties of the corrin nucleus.

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